US ERA ARCHIVE DOCUMENT

UNDATED

#### DATA EVALUATION RECORD

#### DER 5

SHAUGHNESSY No. 041402 COMMON NAME: Molinate

CHEMICAL NAME: S-Ethyl hexahydro-1H-azepine-1-carbothioate

FORMULATION: Not formulated, ring-2-14C-labeled (radiochemical purity 95.6%). DATA REQUIREMENT: Mobility - Leaching and Adsorption/Desorption (163-1)

MRID No: 40749701

Dohn, D.R. 1988. Molinate adsorption/desorption on four soils and one aquatic sediment. Document No. PMS-273; RRC 88-05. Unpublished study performed and submitted by ICI

Americas, Inc., Richmond, CA.

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## **CONCLUSIONS**:

- 1. This study is scientifically valid and can be used towards the fulfillment of data requirements.
- 2. Molinate is mobile in sandy loam, loamy sand, clay loam and clay soils, with Freundlich  $K_{ads}$  values of 0.741-2.04.
- 3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (batch equilibrium) of unaged molinate in sandy loam, loamy sand, clay loam, and clay soils.
- 4. No additional information on the mobility of unaged molinate or the molinate degradates molinate sulfoxide and hexamethyleneimine in soil is needed at this time. If molinate degradates other than molinate sulfoxide and hexamethyleneimine are formed in any laboratory study at greater than 10% of the application rate of molinate, information will be

needed on the mobility (batch equilibrium studies) of those degradates in four soils and one aquatic sediment, of which one will have an organic matter content of < 1% and one will be the same type as used in the aerobic soil metabolism study.

# **METHODOLOGY:**

Keeton sandy loam (0.5% organic matter), Manteca sandy loam (2.2% organic matter), Columbia loamy sand, and Biggs clay soils were sieved (2-mm mesh); a clay loam aquatic sediment from the Colusa canal in California was air-dried and sieved (Table 1). For the preliminary study, the soils were weighed (2.5 g) into duplicate test tubes, then mixed with 10 mL of an aqueous 0.01 M calcium chloride solution containing ring-labeled [14C]molinate (radiochemical purity 95.6%, specific activity 28.8 mCi/mmole, Wizard Laboratories) at approximately 15 ug/mL. Additionally, the [14C]molinate solution was added to two tubes that did not contain soil. The samples were shaken on wrist-action shakers at 20.5°C for 4 hours; the solutions in each tube were centrifuged and sampled hourly, then returned to the shaker. The supernatants were analyzed for total radioactivity using LSC. Based on the resulting data, a soil:solution ratio of 2.5:10 and an equilibration time of 1 hour at 20.5°C was chosen for the definitive study. Also, it was determined that molinate did not adsorb to the walls of the sample tubes and was not volatilized during equilibration.

For the definitive study, 0.01 M calcium chloride solutions containing [ $^{14}$ C]molinate at 0.0159  $\mu$ g/mL, 0.164  $\mu$ g/mL, 1.51  $\mu$ g/mL, and 14.9  $\mu$ g/mL were prepared. The soils and sediment were weighed into duplicate test tubes and mixed with the treated solutions. The soil:solution slurries (2.5 g:10 mL) were shaken for 1 hour at 20.5 °C, then centrifuged, and 8.5 mL of supernatant was decanted from each tube. Aliquots of the supernatants were analyzed using LSC.

To measure desorption, 8.5 mL of a pesticide-free calcium chloride solution was added to each tube to replace the decanted supernatant. The tubes were shaken for 1.5 hours, then centrifuged. Aliquots of each supernatant were analyzed by LSC. Soil that had been equilibrated with 14.9  $\mu$ g/mL of [ $^{14}$ C]molinate was extracted twice with 80% methanol by shaking for 1 hour. The extracts were analyzed using LSC; the extracted soils were air-dried and analyzed using LSC following combustion.

The supernatants from the adsorption and desorption steps, and the methanol soil extracts were analyzed using HPLC with a reverse-phase C-18 column eluted with water:methanol (20:80) and radioactivity and UV (22nm) detection.

### **DATA SUMMARY:**

Based on batch equilibrium studies, [ $^{14}$ C]molinate (radiochemical purity 95.6%), at 0.0159, 0.164, 1.51, and 14.9  $\mu$ g/mL, was determined to be mobile in sandy loam, loamy sand, clay loam, and clay soil:calcium chloride solution slurries (2.5 g soil:10 mL solution) that were equilibrated by shaking for 1 hour at 20°C.

Soil	% OM	Clay	pН	K <sub>ads</sub>	n	r <sup>2</sup>	K <sub>oc(ads)</sub> <sup>1</sup>	K <sub>des</sub>	n	r <sup>2</sup>	K <sub>oc(des)</sub>
Keeton sandy loam	0.5	9.8	7.7	0.741	1.26	0.995	252	1.14	1.34	0.995	388
Columbia loamy sand	1.9	5.8	7.8	1.35	1.12	0.997	121	1.73	1.17	0.990	155
Manteca sandy loam	2.2	10.6	7.5	2.04	1.09	0.999	158	2.70	1.07	0.999	209
Biggs clay	1.7	50.0	5.5	1.95	1.04	0.998	195	2.94	1.09	0.993	294
Colusa Canal sediment	1.3	36.6	7.7	1.57	1.04	0.996	206	1.78	1.17	0.995	233

1  $K_{oc}$ s were calculated using the equation: % organic carbon = % organic matter/1.7.

Adsorption was correlated with % organic matter ( $r^2$ =0.70) and % clay ( $r^2$ =0.93); it was not correlated with pH ( $r^2$ =0.16). Molinate was stable in the samples during the study. At the completion of the study, material balances were 89.3-102% of the applied. Molinate did not degrade in the samples during the study.

## **COMMENTS:**

- 1. The supernatants from the desorption portion of the study were frozen prior to analysis by LSC. However, the analytical values were erratic apparently due to incomplete thawing of the solution. The samples were then completely thawed, mixed, and reanalyzed. The study author stated that the resulting values appeared to be more credible and so reported them in this study. In order to confirm that the samples did not deteriorate during frozen storage, the supernatants from the "no soil" and clay soil samples were thawed and reanalyzed. The study author stated that the reanalysis values were identical to the original measurements. However, no data were provided for review to allow confirmation of the study author's conclusions.
- 2. Soil characteristics values were not corrected for moisture content (footnote 1 to Table 1).
- 3. It was reported that the aquatic sediment was from an area that had been used to collect drainage from rice canals, and therefore had a history of molinate exposure. Analysis of the sediment found a maximum concentration of 3.1 ng molinate per g dry weight of sediment. The lowest concentration of molinate used for equilibration was approximately 20 times that in the soil. The study author stated that it "would not significantly alter the form of the log/log plots" for the sediment.
- 4. Acceptable batch equilibrium studies for the molinate degradates molinate sulfoxide and hexamethyleneimine (MRIDs 41835103 and 41835102, respectively) have been submitted to the Agency.